

This discussion paper is/has been under review for the journal Climate of the Past (CP).
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First continuous phosphate record from Greenland ice cores

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Received: 26 October 2011 – Accepted: 5 November 2011 – Published: 18 November 2011

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

A continuous and highly sensitive absorption method for detection of soluble phosphate in ice cores has been developed using a molybdate reagent and a 2 m liquid waveguide (LWCC). The method is optimized to meet the low concentrations of phosphate in Greenland ice, it has a detection limit of around 0.1 ppb and a depth resolution of approximately 2 cm. The new method has been applied to obtain phosphate concentrations from segments of two Northern Greenland ice cores: from a shallow firn core covering the most recent 120 yr and from the recently obtained deep NEEM ice core in which sections from the late glacial period have been analysed. Phosphate concentrations in 20th century ice are around 0.32 ppb with no indication of anthropogenic influence in the most recent ice. In the glacial part of the NEEM ice core concentrations in the cold stadial periods are significantly higher, in the range of 6–24 ppb, while interstadial ice concentrations are around 2 ppb. In the shallow firn core, a strong correlation between concentrations of phosphate and insoluble dust suggests a similar deposition pattern for phosphate and dust. In the glacial ice, phosphate and dust also correlate quite strongly, however it is most likely that this correlation originates from the phosphate binding to dust during transport, with only a fraction coming directly from dust. Additionally a constant ratio between phosphate and potassium concentrations shows evidence of a possible biogenic land source.

1 Introduction

Phosphorus (P) is an essential macro nutrient important for all living organisms and is present in DNA and bones. Earth's biological systems have been dependent on P since the beginning of life (Filippelli, 2008; Paytan and McLaughlin, 2007). As a result of this dependence P recycling is very efficient in earth's biological systems (Tiessen, 1995). P is one of the limiting nutrients in ecosystems, although the exact extent of limitation

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is intensively debated reaching from the opinion that P is a controlling factor to P being important but not comparable to other macro nutrients such as nitrate (Falkowski et al., 1998; Elser et al., 2007; Worsfold et al., 2008; Tamburini and Föllmi, 2009).

In the earth's crust the mean P concentration is 1200 mg kg^{-1} (Tiessen, 1995). Phosphate (PO_4^{3-}) is generated by weathering and transported to the oceans mainly by rivers, where PO_4^{3-} concentrations are in the range of 2 to 110 ppb (Concright et al., 2000). PO_4^{3-} is most abundant in polar waters and regions of upwelling, where concentrations are generally lower during summer seasons in the surface waters (Concright et al., 2000; Levitus et al., 1993).

As P does not have a gaseous phase it is transported through the atmosphere as particulate matter or as PO_4^{3-} (Graham and Duce, 1982; Baker et al., 2006; Mahowald et al., 2008; Paytan and McLaughlin, 2007). The atmospheric transport as determined in a model study by Mahowald et al. (2008) of P is dominated by mineral dust (82 %), with sea salt, primary biogenic particles, volcanoes and human activity accounting for the remainder. For PO_4^{3-} , the soluble part of total P, mineral dust accounts for only 48 % of the global atmospheric transport, biogenic particles account for 38 %, volcanism accounts for 1.3 % and sea salt merely 2 %, while anthropogenic activity is believed to account for about 14 %. In some countries of mid- and high-latitude Europe (Finland, Norway, Belgium), there is evidence of a high fraction of P in coarse aerosols ($> 1 \mu\text{m}$) having a biogenic origin (Mahowald et al., 2008). Although atmospheric transport only accounts for a small part of the P cycle, it is important for nourishing primary production in the remote ocean (Paytan and McLaughlin, 2007; Mahowald et al., 2008).

Very little information on the amount of P and PO_4^{3-} in the Arctic exists and even less information is available on the concentrations in glaciers. Edwards et al. (2007) measured P on the Greenland ice sheet in snow and firn and found average concentrations of 0.25 ppb P over the last 50 yr. They found a dramatic increase in P during the period 1990–2005 suggested to correspond to increased forest fire burning. Analysis of glacier run off from smaller glaciers show P concentrations between 0.31 ppb and 145 ppb (Chillrud et al., 1994; Tockner et al., 2002) and the soluble fraction of P was

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found to be low, 0.2 % to 4.3 %, in a study by Hodson et al. (2004) looking at particulate melt water from glaciers in France, Pakistan, Svalbard and Sweden.

The cycling of P is suggested to vary greatly over glacial-interglacial cycles (Mahowald et al., 2008; Filippelli, 2008). In glacial times sea level changes have exposed shelf areas allowing P deposition on shelves to be re-introduced to the global cycle. This so-called shelf nutrient hypothesis has been observed in marine records (Tamburini and Föllmi, 2009; Filippelli, 2008; Delaney, 2000; Elderfield and Rickaby, 2000). In the Holocene a general trend of increasing mineral P has been observed as a sign of cooling conditions in alpine regions, but several short-lived changes have been observed as well (Filippelli et al., 2006). In recent times, the natural cycling of PO_4^{3-} has been impacted by anthropogenic activities, such as the use of P as a fertilizer (Schlesinger, 1991; Tiessen, 1995; Diaz and Rosenberg, 2008; Oelkers and Valsami-Jones, 2008; Filippelli, 2008) and forest fire burning (Filippelli, 2008; Paytan and McLaughlin, 2007; Bolin et al., 1981).

Over geological time scales P is believed to be the limiting nutrient in oceans. The increased level of Fe believed to be transported to the ocean as an effect of the general increased dust level in the atmosphere during glacial times, supports denitrification processes in the oceans by increasing levels of cyanobacteria which fix Nitrogen. Eventually the amount of phytoplankton would be PO_4^{3-} limited, thus carbon sequestration would have been PO_4^{3-} limited, too (Falkowski et al., 1998; Paytan and McLaughlin, 2007).

Ice cores provide an archive of past climate in high temporal resolution. Greenland ice cores cover the last glacial cycle (NGRIP members, 2004), whereas Antarctic ice cores archive almost a million years of past climate (EPICA community members, 2004). During the second half of the last glacial period, Greenland ice cores show evidence of important climate variability with generally colder climate conditions, stadial periods (GS), being abruptly interrupted by milder interstadial periods (GI), the so-called Dansgaard-Oeschger events.

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Such past climate conditions can be reconstructed from the impurities in Greenland ice cores. Insoluble dust provides information on atmospheric transport patterns and dust source regions (Ruth, 2005; Svensson et al., 2000), sea salt components are related to the oceanic environment and wind speed (de Angelis et al., 1997; Fischer et al., 2007), sulphate concentration peaks often reflect volcanic activity (Zielinski et al., 1996), and biogenic activity, such as forest fires or marine bioproductivity can be detected as well (Fuhrer et al., 1996) as is the case for anthropogenic impacts (McConnell et al., 2007a,b). Furthermore, there is a pronounced seasonality in the deposition of these impurities-insoluble dust is regularly deposited in the boreal spring, forest fire proxies in summer and sea salts in winter (Legrand and Mayewski, 1997).

In general, the coldest periods during the glacial have the highest loads of almost all impurities. Over stadial-interstadial cycles concentrations change by a factor of 10 for dust proxies, while sea salt proxies vary by a factor of 3 (Hansson, 1994; Mayewski et al., 1997). The dust load is especially high in the period around 23–26 ka, probably due to a combination of lowered sea level, increased winds, and dry atmospheric conditions (Ruth, 2005; Maher et al., 2010).

In this pilot study, PO_4^{3-} analyses have been performed on two North Greenland ice cores, a map is provided in Fig. 1. Preliminary measurements were performed on a shallow firn core (76.45° N, 44.77° W, 2771 m a.s.l.) drilled in 2007 during a traverse expedition between the NGRIP and NEEM ice core drilling sites. However only a few sections between 6 m and 34 m depth were analysed. Later, glacial sections of the NEEM ice core (77.45° N 51.0° W, 2484 m a.s.l.), a major international deep drilling project initiated in 2007, were analysed in the field in 2010. They cover the depth 1607.7 m to 1764.9 m corresponding to the late glacial period (~22 to 37 ka).

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2 Experimental methods

2.1 Phosphate detection for a CFA-set up

In recent times Continuous Flow Analysis (CFA) has become a widely applied method for detection of dust and chemical impurities in ice cores, mainly because of the high resolution provided by the method as well as improved contamination control and sample throughput (Sigg et al., 1994; Röthlisberger et al., 2000; Kreutz, 2006).

For the shallow firn core analyses the new PO_4^{3-} detection system was connected to the existing CFA system in Copenhagen (Bigler et al., 2011). For the NEEM ice core analyses the system was attached to the Bern CFA setup (Kaufmann et al., 2008) in the field. In both cases an air-segmented continuous flow spectrophotometric method was implemented for the determination of PO_4^{3-} concentrations (Fig. 2). The flow rates were different between the two setups, as the Copenhagen set-up is optimized for high resolution measurements, while the Bern set-up is optimized to measure many species efficiently in deep ice cores (Bigler et al., 2011).

The PO_4^{3-} detection system is adapted from the method by Murphy and Riley (1958) that was later optimized by Zhang et al. (1999) and Zhang and Chi (2002). A 12-molybdophosphoric acid is formed from the reaction of PO_4^{3-} in the sample with molybdate in an acidic solution in the presence of potassium antimony tartrate. The 12-molybdophosphoric acid is subsequently reduced by ascorbic acid to a phosphomolybdenum blue complex. The absorbance of the phosphomolybdenum blue complex is measured at 710 nm by a 2000S spectrometer, with the sample illuminated by a DT-MINI-2GS deuterium tungsten halogen light source (both Ocean Optics, Dunedin FL, USA). To enhance the limit of detection (LOD), absorbance was measured in a two metre liquid waveguide capillary cell (LWCC, Ocean Optics, Dunedin FL, USA) with an inner volume of only 0.5 ml as suggested by Zhang and Chi (2002).

The sensitivity of the method was further increased by heating the mixed reagents to 65°C, although sample heating increases the risk for interferences resulting from the production of precipitates of silicate and arsenate (Zhang and Chi, 2002; Gimbert

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and Worsfold, 2007; Nollet, 2007; Ma et al., 2009). Such interferences are possible, as these ions react with molybdenum blue to create the same blue colour as the reaction with PO_4^{3-} . Zhang et al. (1999) estimated the extent of the potential silicate interference using the mean crustal silica abundance: assuming the same abundance for dust (27.7% by weight), the maximum concentration of silicate in ice cores during the glacial maximum is $20\text{ }\mu\text{M}$. As this would result in an apparent PO_4^{3-} concentration of $0.6\text{ }\mu\text{M}$ (0.6 ppt), such an interference would not affect our results significantly. Arsenate is probably not present in ice cores in quantities large enough to perturb the measurements of PO_4^{3-} , but in such a case thiosulfate could be added to the reagent to preferentially react with Arsenate (Zhang and Chi, 2002). Thiosulfate addition was not done in this study.

Various flow rates, mixing lengths, detection wavelengths, spectrum integration, and filter types were tested and optimized to increase detection of low concentrations of PO_4^{3-} . Optimal flow rates, used for the shallow firn core analyses, were found to be 1.7 ml min^{-1} for sample, 0.15 ml min^{-1} for reagent and buffer and 0.20 ml min^{-1} for air, which was introduced to limit sample dispersion. It is recommended that mixing occurs over at least 3 m of PFA tubing of a diameter of 0.5 mm, in a heat bath with a steady temperature of about 65°C . In front of the detection cell air was removed using a sealed debubbler (Bigler et al., 2011). Final LOD in such a set up was 0.1 ppb. The flow rates applied for the detection of the NEEM ice core analyses in Greenland were 0.9 ml min^{-1} for sample, 0.08 ml min^{-1} for reagent and buffer and 0.15 ml min^{-1} for air and due to the set-up at NEEM the mixing length was increased to 5 m at approximately 17°C and 1 m heated to 65°C .

A filter was introduced to remove particulates that would otherwise completely obscure the LWCC. The filter consists of a 3 cm column with an internal volume of about $2\text{ }\mu\text{l}$, 2/3 filled with glass wool, which succeeded in removing essentially all dust. The filter was located just prior to the LWCC to make sure that all soluble PO_4^{3-} attached to dust had time to react before detection. The filter was changed regularly depending on the dust content of the sample analysed: for the shallow firn core the filter did not

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require replacement, but for the NEEM campaign, it was changed regularly. A new filter was used after the analysis of each 9 m section of interstadial ice and more often, up to every 2 m, when analysing impurity-laden stadial ice.

2.2 Reagents and standards

5 All samples and reagents were stored in polypropylene bottles (Nalgene Corp., Rochester NY, USA). All reagents used were of analytical grade, purchased from Merck (Darmstadt, Germany). The reagents are similar to the ones described in Zhang and Chi (2002) except for the stock ammonium molybdate, which had a higher concentration. Stock antimony potassium tartrate solution was prepared by dissolving 0.3 g of
10 antimony potassium tartrate in 100 ml of deionized water. The solution was stored in a dark bottle in a refrigerator. Stock ammonium molybdate solution was prepared daily by dissolving 0.37 g of ammonium molybdate in 25 ml of 5N H_2SO_4 solution, then adding 5 ml stock antimony potassium tartrate solution, and diluting to 100 ml with deionized water. Ascorbic acid solution was prepared daily by dissolving 0.5 g of ascorbic acid and 7 g of sodium dodecyl sulfate in 100 ml of deionized water. A stock solution
15 of PO_4^{3-} (999 ppm, Merck, Darmstadt, Germany) was diluted to make standards.

3 Samples and data processing

All measurements were calibrated using PO_4^{3-} standards with a linear fit between absorption and concentration, which is appropriate for the concentrations found in ice
20 (Zhang and Chi, 2002). For the shallow firn core five standards were measured for every 2.75 m of sample, while only three standards were run for the NEEM ice core and only after every 4.4 m of sample.

For the NEEM analyses, variability in the baseline and system sensitivity were observed predominantly as a result of the higher impurity content of the samples. Higher
25 PO_4^{3-} concentrations and to some extent the low flow and thus longer mixing time for

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the reaction caused some coating of the tubing – observed as a steady colour change of the tubing. This behaviour was not observed during the shallow firn core analyses. This coating was possibly enhanced by a roughening of cell walls due to higher dust load. Flushing the tubing with solutions of methanol, 5 % hydrochloric acid, or sodium hydroxide did not remove the coating. Furthermore, the large amount of dust in the glacial samples required the filter to be changed at least once a day. It is possible that PO_4^{3-} , entrained onto dust trapped in the tubing and/or the filter, may have gradually increased the concentration of PO_4^{3-} thus causing a lowered baseline over the course of each measurement. To compensate for this a linear correction of the baseline was made from start to end of each measurement (Fig. 3). The baseline correction procedure introduced an additional uncertainty to the NEEM measurements: while normally less than 2 ppb for each run (110 cm), these baseline changes were occasionally up to 4 ppb (see Table 1).

The shallow firn core measurements show brief contamination spikes at the beginning and end of each run, most likely related to handling of the ice sample. This was removed later at the signal processing stage. Such a contamination was not visible for the NEEM ice core, because of the higher concentrations detected in the ice and more careful sample preparation procedures.

The depth resolutions for the shallow firn core and the NEEM ice core analyses are estimated from spectral analysis to be 1.3 cm and 5.7 cm, respectively. The lower depth resolution for the NEEM ice core analyses was due to the lower flow rate and increased sample mixing time as well as due to increased coating due to higher PO_4^{3-} concentrations.

For the processing of the shallow firn core melting speed data were used to correct for melt rate variations, while the NEEM ice core was processed assuming a linear melt rate, which does not cause large errors because of the high mixing already smoothing the signal. Figure 3 shows examples of raw data and calibrated data detected in the two different set-ups. The signal to noise ratio is very different for the two because of the much higher concentrations found in the NEEM ice core.

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Greenland ice cores are dated to high accuracy using annual layer counting and fixed tie-points such as volcanic layers that are common to several ice cores, as well as linking to records from other palaeoarchives (Andersen et al., 2006; Rasmussen et al., 2006).

The shallow firn core was dated using a Heron-Langway model tuned to fit the density profile and the Laki (1783 AD) and Tambora (1815 AD) eruptions that were identified through electrical conductivity measurements. An accumulation rate of 0.181 m ice equivalent per year was used.

To enable comparisons between NEEM data and NGRIP potassium record, the NGRIP records were transferred to NEEM depths using stratigraphic fix points at the onsets of Dansgaard-Oeschger events. This same method has been used to transfer the NGRIP chronology to NEEM. Potassium records from the GISP2 ice core were directly transferred to NEEM depths using the GISP2 dating for fix points (Mayewski et al., 1997).

4 Shallow firn core

From a shallow firn core covering the past 120 yr, phosphate has been determined for selected intervals. 7.75 m of firn were measured, covering the depths 6.05 to 7.15 m, 8.80 to 10.45 m and 28.05 to 33.50 m as shown in Fig. 4. The mean concentration level was 0.32 ppb with a standard deviation of 0.27 ppb and a maximum value of 4.18 ppb. This is on the same order of magnitude as the 0.25 ppb P concentrations determined in Greenland snow (71.4° N, 44° W and 65° N, 44.9° W) using ICP-MS (Edwards et al., 2007).

The PO_4^{3-} concentration is strongly correlated with dust suggesting similar sources and/or similar transport processes.

In the shallow firn core, PO_4^{3-} shows no apparent seasonal variation. Although PO_4^{3-} concentrations are somewhat higher in spring and winter, with means of 0.44 ± 0.24 ppb (standard deviation) and 0.41 ± 0.28 ppb, respectively, summer

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(0.34 ± 0.19 ppb) and autumn (0.27 ± 0.17 ppb) concentrations are identical within the observed error range. The seasonality was evaluated by splitting the year in four equal parts and determining each year based on an estimation of annual layer thickness as defined by the NH_4^+ summer peak. Seasonal variability in the potential sources of phosphate were considered in an attempt to identify the greatest contributors. Of the oceanic sources, 2 to 3 times higher PO_4^{3-} concentrations are observed every winter in surface waters of the North Atlantic and North Pacific between 40° and 70° N. Concrigh et al. (2000) explained that this winter enrichment is due to the general circulation in the oceans. As a similar pattern was not observed for the firn core samples, it is likely that sea salt emissions are not the main PO_4^{3-} source. To some degree the PO_4^{3-} better resembles the behaviour of dust, with a steady spring maximum. A linear fit between PO_4^{3-} and dust is best in autumn ($R^2 = 0.91$) and spring ($R^2 = 0.81$), while for the winter ($R^2 = 0.73$) and summer ($R^2 = 0.43$) the fits are weaker. As the gradients of the fits vary from about 0.3×10^4 in autumn, rising in the winter, 0.7×10^4 , and summer, 0.8×10^4 and showing the highest inclination in springtime 1.6×10^4 it supports different origins of dust over the year or more likely, additional phosphate sources in some seasons. It is unclear how a biogenic phosphate signal may change on seasonal scales. Mahowald et al. (2008) suggested that there would be no major seasonal changes for a biogenic PO_4^{3-} source in the tropics, but does not exclude the possibility of seasonal variations in higher latitudes, with a minimum in wintertime.

The firn PO_4^{3-} record also shows some spikes coinciding with ammonium (NH_4^+), but not with dust (Fig. 4), suggesting occasionally a common source of the two, for example a biogenic signal. It is unlikely that the coinciding spikes of NH_4^+ and PO_4^{3-} could be evidence of a terrestrial fertilizer signal, since such a signal would be expected annually and the spikes are only visible in some years.

The results found in the 19th century firn at depths of 28 m to 34 m (approximate 1880 to 1920 AD) are compatible with more recent snow at depths of 6 m to 11 m (1978 to 1994 AD) suggesting there is minimal influence to atmospheric PO_4^{3-} from modern anthropogenic activities.

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5 NEEM deep ice core

The NEEM PO_4^{3-} record is shown in Fig. 5 together with records of δD , insoluble dust, Ca^{2+} , NH_4^+ , Na^+ from NEEM measured using CFA as well as K^+ from the NGRIP and the GISP2 ice cores measured by Ion Chromatography (IC). NGRIP is only 365 km from NEEM and so is likely to provide levels of K^+ comparable to those expected at NEEM. Due to the presence of spikes in the NGRIP K^+ record, GISP2 data was also included.

The NEEM PO_4^{3-} record covers sections within glacial interstadial 2 to 8 (22.4–36.8 kyr BP). In the mild interstadial sections (B) PO_4^{3-} levels are in the range 0.3 to 12 ppb with mean values between 0.7 and 2.1 ppb (Table 1). In the glacial stadials (A) the level is consistently higher with concentrations between 1.9 and 59 ppb and the mean of the sections covered in GS (A) showed concentrations from 6.4 to 24.1 ppb. To first order PO_4^{3-} concentrations are thus negatively correlated to the temperature proxy δD , with higher PO_4^{3-} concentrations during colder climatic periods.

The ratio between PO_4^{3-} concentrations in recent snow (the shallow firn core analysis) and those in the cold GS in the NEEM ice core is up to 200, while the mild GI show changes by a factor 16 making PO_4^{3-} comparable to other dust proxies (Steffensen, 1997; Ruth et al., 2003; Ruth, 2005; Maher et al., 2010).

A rough estimate of the maximum amount of PO_4^{3-} that could theoretically originate from dust was calculated using the mean amount of dust in the coldest period from the GRIP ice core in the period GS3 ($7600 \mu\text{g}_{\text{dust}}/\text{kg}_{\text{ice}}$; Steffensen, 1997) and the global mean of P in dust (1200 mg kg^{-1} ; Tiessen, 1995). Even if one assumes that P is 100 % soluble, unlikely given that Hodson et al. (2004) found a soluble P fraction of less than 2 %, we find that at most only 5.8 ppb PO_4^{3-} ($\sim 24\%$) could be explained by dust deposition in the period of GS3. Another way of estimating the theoretical amount of P arriving to the ice is using the same procedure, but estimating the dust weight from the values in Table 1 using the rough relationship found in Lambert et al. (2011), namely

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that the mass of dust relative to ice (M) in ng g^{-1} is given by $M = 10^{(\log_{10}(D)-1.14)}$, where D is the dust in particles ml^{-1} . In this case the amount of dust is $1913 \mu\text{g}_{\text{dust}}/\text{kg}_{\text{ice}}$ for the period A1 positioned in GS3 corresponding a theoretical level of PO_4^{3-} from dust of merely 2.3 ppb ($\sim 10\%$), when assuming all P arriving as PO_4^{3-} . It is not surprising that the level is lower when calculating it based on NEEM data since the GRIP ice core is from Central Greenland, where dust levels are higher. The GRIP value is presented to give an absolute maximum value of the theoretical arrival of PO_4^{3-} originating from dust sources in GS3. For the remaining periods the amount of PO_4^{3-} that theoretically could arrive from dust determined using the Lambert method varies between 6 % and 43 %. This is a clear indication that dust inputs alone are insufficient to account for the PO_4^{3-} concentrations observed in NEEM ice. The theoretical level of PO_4^{3-} arriving from dust sources to the ice is thus much lower than the percentage of global mean PO_4^{3-} arriving from dust sources determined in the model by Mahowald et al. (2008), who applied a solubility fraction of 10 %. It should also be noted, that the total P level in dust in aerosols vary by about 30 % globally (Mahowald et al., 2008).

In order to further consider the potential sources of PO_4^{3-} present in NEEM ice, evaluations were made of correlations between PO_4^{3-} and other impurities reported in Greenland ice cores. Most impurities generally do correlate to some degree during the last glacial. Figure 6 presents high resolution data from depths 1703.30 to 1707.75 m, with a clear correlation between PO_4^{3-} , dust and soluble Ca^{2+} . This correlation occasionally breaks down, with some dust spikes having no counterpart in PO_4^{3-} and vice versa. The relationship between PO_4^{3-} and dust was further investigated by comparing 110 cm mean values as shown in Fig. 7. This comparison shows a high correlation (0.83) based on 110 cm means, but also implies additional PO_4^{3-} sources, especially when recalling the potential PO_4^{3-} contribution calculated from dust sources. Other potential explanations for variability in PO_4^{3-} – dust correlations are different sources of dust with variable soluble fractions of P and/or different atmospheric transport mechanisms. It is likely that PO_4^{3-} due to its high negative charge binds to positively charged

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dust particles in the atmosphere and thus an increase of dust (or Ca^{2+}) as observed during the glacial stadials will enhance the efficiency of PO_4^{3-} transport to the ice sheet, independent of source changes of PO_4^{3-} . Based on the mass-balance calculations described earlier, it is unlikely that more than about half of the PO_4^{3-} found in the NEEM ice core originates from dust, although it is likely that close to all PO_4^{3-} is co-deposited on the ice with dust.

The amount of sea salt derived PO_4^{3-} was evaluated from the Cl^- level in the NGRIP ice (measured by IC) assuming that its only source was sea salt and using the fractionation coefficient between Cl^- and PO_4^{3-} in sea salt, $R_{\text{seasalt}} = 5.68 \times 10^{-6}$ (Gianguzza et al., 2002; Concright et al., 2000). From this calculation we found that the sea salt PO_4^{3-} contribution was at most 0.001 ppb PO_4^{3-} and thus it is unlikely that there is any significant contribution from sea salt to the PO_4^{3-} seen in the NEEM ice core. In a multi-variable box model approach to the soft tissue carbon pump by de Boer et al. (2010) the PO_4^{3-} level in the surface ocean at 70°N is estimated to change from a concentration of 49 ppb during interglacial to 80 ppb during glacial periods excluding atmospheric transport. However since Cl also doubles its concentration (0.25 to 0.5 g kg^{-1} , Adkins et al., 2002) the higher levels of PO_4^{3-} in surface waters do not significantly increase the calculated contribution arriving from sea areas. Na^+ , also a sea salt proxy though not an unambiguous one, has a correlation with PO_4^{3-} of 0.75, based on 110 cm means. In high resolution close up comparisons (Fig. 6) concentrations of Na^+ and PO_4^{3-} follow each other, but the position of spikes in the PO_4^{3-} follow dust and Ca^{2+} better. Further Na^+ lacks the prominent spikes found in PO_4^{3-} during the last glacial maximum, and A7 has too low a Na^+ concentration with respect to PO_4^{3-} .

In summary the combined amounts of PO_4^{3-} theoretically arriving from sea salt and dust source areas are insufficient to explain the amount of PO_4^{3-} detected in NEEM ice, thus it is likely that other sources such as biogenic emissions or volcanism are substantial contributors to the PO_4^{3-} budget.

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The likelihood of PO_4^{3-} inputs originating from biogenic activity was evaluated by comparison to potassium records in NGRIP and GISP2 ice cores – K^+ concentrations are not yet available from NEEM. The comparison of two measurement techniques (Continuous CFA; Discrete IC) applied to different ice core records (respectively: NEEM; NGRIP and GISP2) introduces the possibility of bias. Downscaling is required to compare continuous measurements to discrete measurements, and different levels of impurities are sure to be found at different locations across the Greenland ice cap. From these caveats we can attempt a preliminary evaluation of phosphate sources but a more refined evaluation will not be possible until K^+ data are available from NEEM ice.

Initial comparison of NEEM PO_4^{3-} and NGRIP K^+ produced a weak correlation (0.58), due to the presence of excess K^+ spikes in the NGRIP record. These spikes had a strong influence on the low PO_4^{3-} concentrations. To test whether such spikes were anomalous, the GISP2 K^+ record was also evaluated and used to determine which of the excess spikes in the NGRIP record could be discounted. After removing the 9 largest spikes in the NGRIP K^+ record, the correlation grew to 0.84 (Figs. 5 and 7). It has been suggested that simultaneous enrichments in P and K may be an indicator of aerosols of biogenic origin (Graham et al., 2003; Mahowald et al., 2008). The ratios between K^+ and PO_4^{3-} vary for sea salt ($0.03\text{--}4 \times 10^{-4}$), dust (0.05–0.10) and biogenic material (0.01–5.5) (Concright et al., 2000; Basile et al., 2003; Enghag, 1998; Graham et al., 2003). Comparing these ratios with those found between potassium from NGRIP or GISP2 and PO_4^{3-} from NEEM in ice (~ 1), it seems that the ratio found in the ice best follows a biogenic signal. It should however be noted that the literature on the ratio between P and K was very limited and that the biogenic ratio is based solely on land source observations.

The NH_4^+ and PO_4^{3-} records obtained in the NEEM ice core correlate by 0.75. Looking at the high resolution plot in Fig. 6, the NH_4^+ and PO_4^{3-} records appear to follow each other. In Fig. 7, however, the correspondence seems less convincing, especially for the low levels of NH_4^+ . The correlation between NH_4^+ and PO_4^{3-} could support a common

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biogenic source. NH_4^+ is believed to originate from from soil and vegetation and to contain spikes originating from forest fire burning in North America (Fuhrer et al., 1996).

The shelf nutrient hypothesis is supported by the level of PO_4^{3-} detected in the ice cores. The level is highest during the colder periods, in which the sea level is lower and thus more of the shelf area is exposed, however this is also the case for many of the other impurities. Closer comparison to the sea level changes determined by Sidall et al. (2010), did not clarify the matter because the record of detected PO_4^{3-} is too short for a reliable comparison, but more importantly due to the variability between different sea level estimates on short time scales.

The increased amount of PO_4^{3-} in glacial ice suggests that the transport of P was greater in glacial times, and thus the amount of fertilization of remote ocean sites most likely was also higher, potentially supporting a greater amount of primary productivity in the oceans. Unlike high nutrient low chlorophyll (HNLC) waters, which are studied in detail for the possibility of fertilization by iron and other macro nutrients (Parekh et al., 2008), much larger expanses of open ocean are instead limited by macro nutrients such as P, and thus may contribute significantly to glacial draw-down of CO_2 (Falkowski et al., 1998; Lüthi et al., 2008; de Boer et al., 2010). However the atmospheric transport of nutrients are often not included or only included for some species when modelling past climate. And when included the nutrients are often determined based on the transport of dust. This study shows that the PO_4^{3-} concentrations found in the NEEM record exceed the levels that would be expected if dust were the only PO_4^{3-} source. The high levels of PO_4^{3-} reported here for the past glacial period demonstrates the continued importance of observational data for the accurate modelling of glacial CO_2 draw-down.

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The first high-resolution continuous PO_4^{3-} record from a Greenland ice core has been obtained using an adapted version of the method suggested by Zhang and Chi (2002), which differs from other molybdenum blue methods by the use of a 2 m LWCC. A filter was introduced to avoid optical interferences from dust and a heat bath was implemented to enhance the sensitivity of the method. Using this set-up concentrations down to 0.1 ppb PO_4^{3-} were detected.

PO_4^{3-} detected in a shallow firn core shows a weak seasonal pattern with maxima in winter and spring time and a minima in autumn. In the recent years the level was only 0.32 ppb. No change in PO_4^{3-} concentrations was observed from the early to late 20th century.

Higher PO_4^{3-} concentrations are found in glacial NEEM ice, demonstrating a negative correlation with temperature. Glacial stadials have in mean PO_4^{3-} levels varying between 6.4 and 24.1 ppb with the highest level of 59 ppb occurring in stadial 2 in coincidence with the periods of the highest dust loads. The glacial interstadial periods have much lower mean concentration level of 0.7 and 2.1 ppb. For the detection of ice with high PO_4^{3-} concentrations (glacial stadials) one could consider using a shorter LWCC, for example of about 50 cm. According to Adornato et al. (2007) that should still be sufficient to get a LOD of 1.0 ppb PO_4^{3-} .

A high correlation of PO_4^{3-} and dust concentrations was found in both the shallow firn core and the older NEEM ice core, with concentration changes between glacial and interglacial climates on the same order of magnitude as for other dust proxies. The high correlation to dust is partly due to dust being a source for up to half of the PO_4^{3-} and partly due to dust particles acting as a transport and/or deposition agent for the PO_4^{3-} originating from other sources. Strong correlations between NEEM PO_4^{3-} and NGRIP K^+ also suggest a common source, possibly terrestrial biogenic emissions. High resolution measurements of K^+ in NEEM ice are essential for the verification of this correlation and could help to determine their dominant source(s). Some common

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peaks between PO_4^{3-} and NH_4^+ in the firn record also suggest a biogenic source of PO_4^{3-} .

The increased level of PO_4^{3-} found in glacial times suggest that transport of PO_4^{3-} in the atmosphere must have been higher, causing an increased fertilization of remote oceans. The higher level of PO_4^{3-} also supported by the shelf nutrient hypothesis.

Acknowledgements. This work is a contribution to the NEEM ice core project, which is directed and organized by the Center of Ice and Climate at the Niels Bohr Institute and US NSF, Office of Polar Programs. It is supported by funding agencies and institutions in Belgium (FNRS-CFB and FWO), Canada (NRCan/GSC), China (CAS), Denmark (FIST), France (IPEV, CNRS/INSU, CEA and ANR), Germany (AWI), Iceland (Rannís), Japan (NIPR), Korea (KOPRI), The Netherlands (NWO/ALW), Sweden (VR), Switzerland (SNF), UK (NERC) and the USA (US NSF, Office of Polar Programs).

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Table 1. Mean values from the NEEM ice core for PO_4^{3-} as well as σ , the uncertainty introduced by baseline correction and the variability detected when measuring standards, δD , Conductivity and Dust. The data has been determined for periods A within the cold glacial stadials (GS) and B warmer glacial interstadials (GI) defined by the depth intervals in rows 3 to 6. Means were calculated only for the depths where PO_4^{3-} was measured.

Period	Within period	depth interval (m)	PO_4^{3-} (ppb)	σ (ppb)	δD (‰)	Cond ($\mu\text{S}/\text{cm}$)	Dust $\times 10^3$ (Part. $> 1\mu\text{m}$)
A1	GS3	1607.70–1621.82	24.1	2.8	-339	3.03	159.2
A2	GS3	1623.16–1626.25	10.5	1.0	-341	2.10	114.4
B1	GI3	1639.59–1640.62	2.0	0.8	-298	1.04	16.5
B2	GI4	1651.70–1654.00	2.1	0.5	-312	1.09	21.2
A3	GS5	1657.20–1661.49 and 1662.71–1666.96	13.2	1.2	-348	3.16	150.8
A4	GS5	1675.91–1678.01 and 1679.20–1680.41	7.7	2.2	-341	2.24	98.8
B3	GI5	1684.72–1689.02	0.7	0.4	-312	0.99	14.5
A5	GS6	1691.32–1693.37 and 1694.73–1695.50	6.4	1.1	-339	2.14	94.4
B4	GI6	1697.90–1702.24	1.6	0.2	-309	1.06	13.9
A6	GS7	1703.41–1709.87	11.7	2.0	-335	2.04	81.3
B5	GI7	1717.73–1720.9	1.7	0.6	-304	0.96	11.9
A7	GS8	1724.31–1728.6	22.2	4.1	-335	1.95	82.5
B6	GI8	1754.00–1756.11 and 1757.29–1758.26	0.8	0.5	n/a	1.01	9.8
A8	GS9	1759.80–1764.94	8.2	1.4	n/a	1.88	76.6

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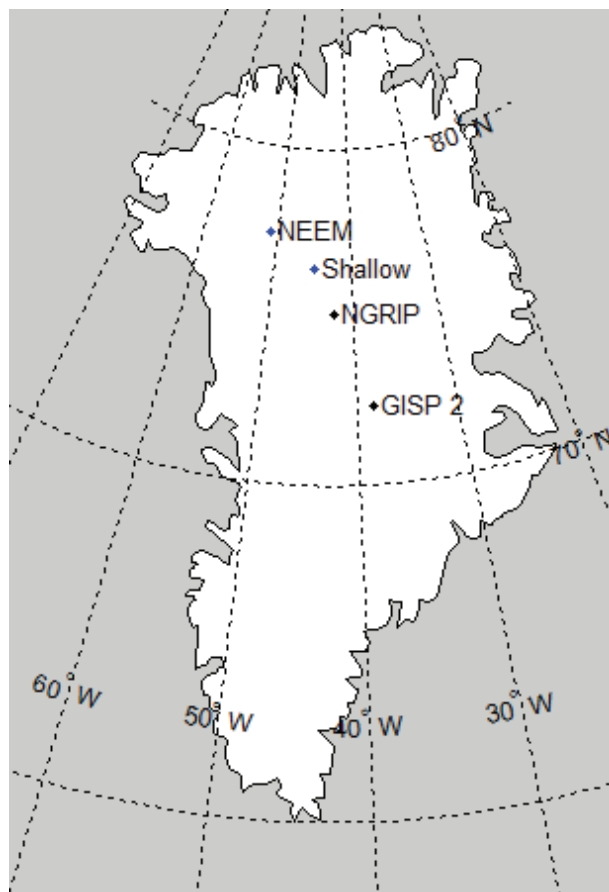



Fig. 1. Position of the ice cores used in this study. In blue the ice cores for which phosphate has been detected.

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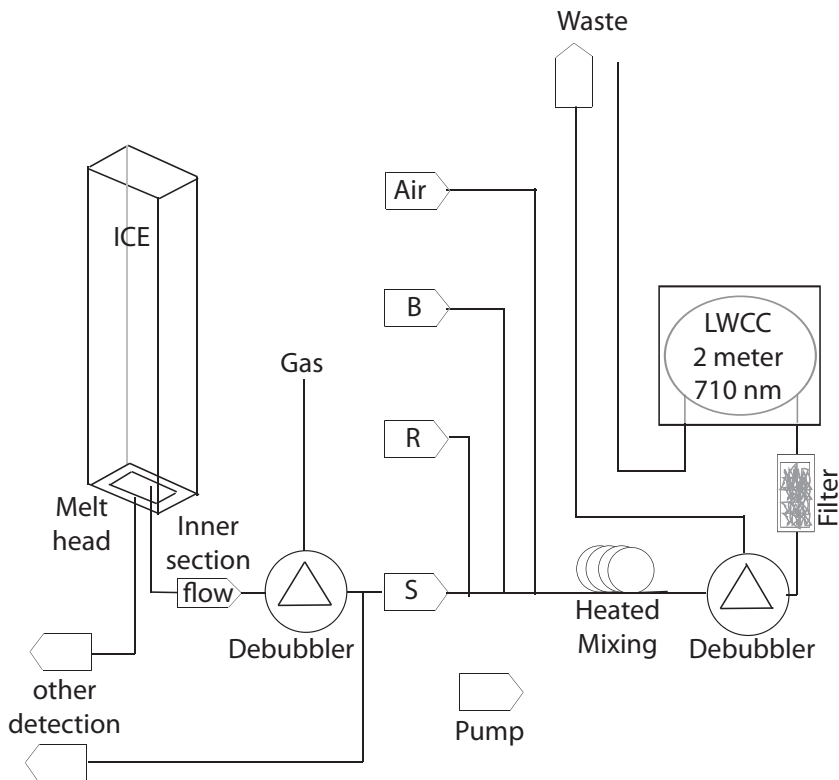


Fig. 2. The continuous flow setup for PO_4^{3-} detection. Ice is melted on a melt head in a freezer kept at -20°C . The melt water is split between an inner part and an outer part that is discarded. The inner part is de-bubbled and split for different types of detection, of which only the PO_4^{3-} line is shown here. The sample (S) is mixed with reagent (R), buffer (B) and air (to avoid dispersion) then passed through a 3 m heated (65°C) mixing coil before a second debubbler removes the air. The sample is filtered to avoid optical interferences. Absorption at 710 nm is measured in a 2 m Liquid Waveguide Capillary Cell (LWCC).

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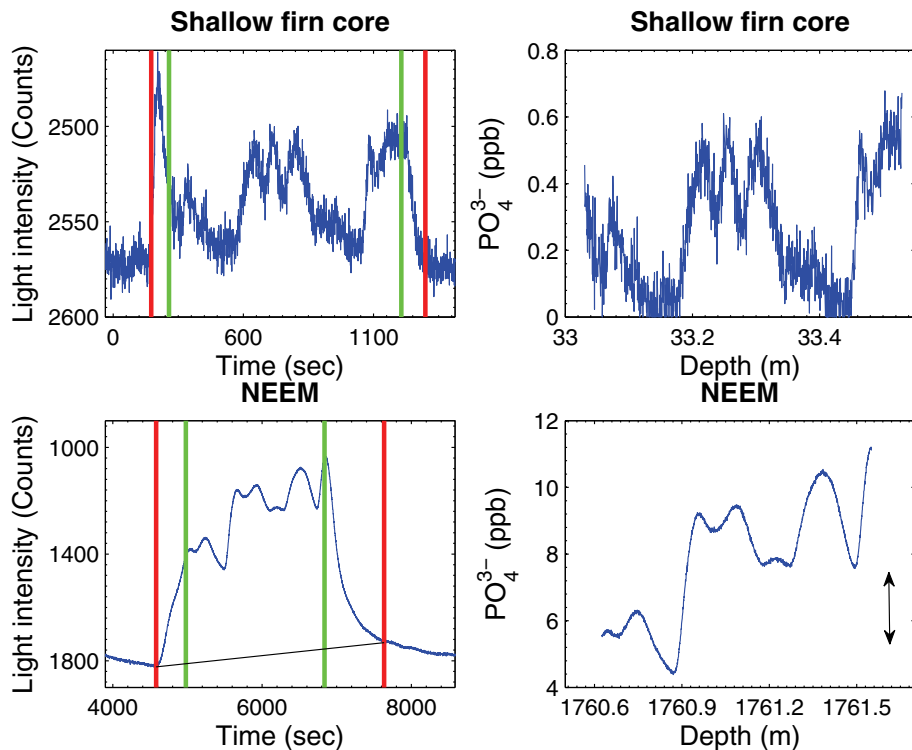


Fig. 3. Raw and calibrated PO_4^{3-} measurements from a shallow Greenland firn core and the NEEM ice core. Raw PO_4^{3-} data (left) are shown as light intensity (reversed scale) as a function of time. In the beginning and end of each sample there is a transition between baseline and sample which is removed (vertical lines). Calibrated datasets (right) are shown as PO_4^{3-} concentrations on a depth scale. The different light intensities between uncalibrated shallow firn and NEEM ice measurements reflect the different experimental conditions between the laboratory and field. The concentration uncertainty due to baseline correction is indicated by the double arrow.

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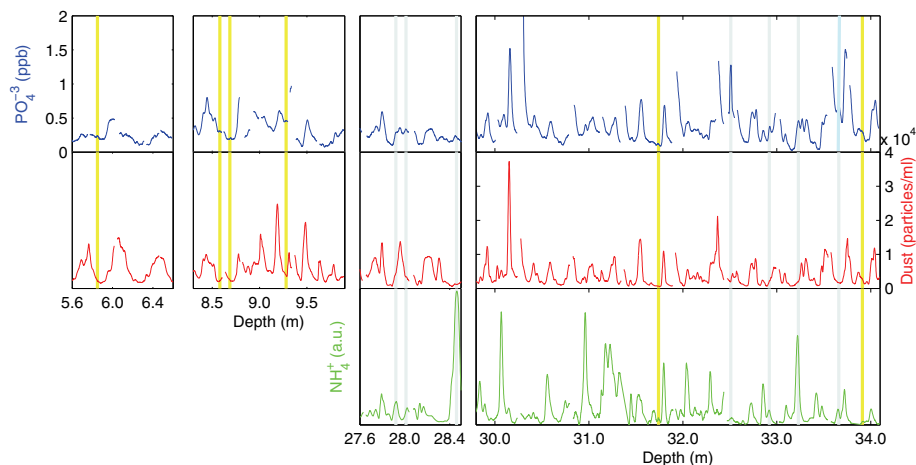


Fig. 4. Shallow firn core measurements from the depth span of 5.6 m to 34.1 m covering the period 1994 AD to 1912 AD. The uppermost curve shows PO_4^{3-} (blue), the middle curve is dust (red) and the lowermost curve shows ammonium (green) measurements. The ammonium record shown here was not calibrated so it is reported qualitatively. The vertical yellow lines mark small bumps in the PO_4^{3-} , which were not matched by dust. The vertical light blue lines mark PO_4^{3-} variations which were matched by variations in ammonium but not dust.

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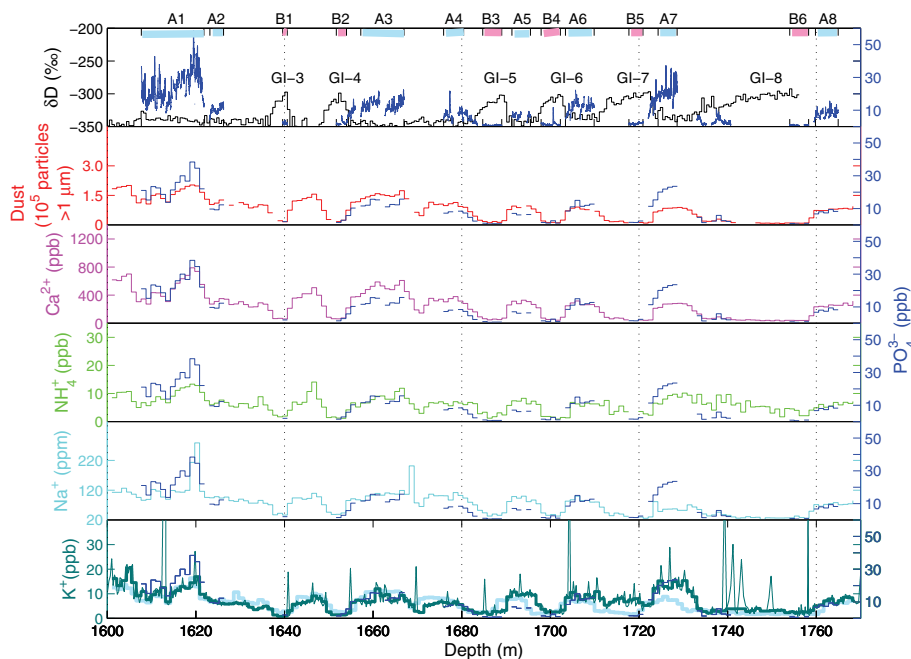


Fig. 5. PO_4^{3-} from NEEM (blue) plotted with δD (black) in high resolution in the top panel, and as bag means with dust (red), Ca^{2+} (pink), NH_4^+ (green) and Na^+ (light blue) all from NEEM. In the bottom panel NEEM PO_4^{3-} is plotted with K^+ from NGRIP original (dark thin cyan) and means without spikes (dark thick cyan) and GISP2 (light thick cyan) (Mayewski et al., 1997) transferred to the NEEM depth scale. Note that all plots have the same PO_4^{3-} and depth scales but different scales for the individual species.

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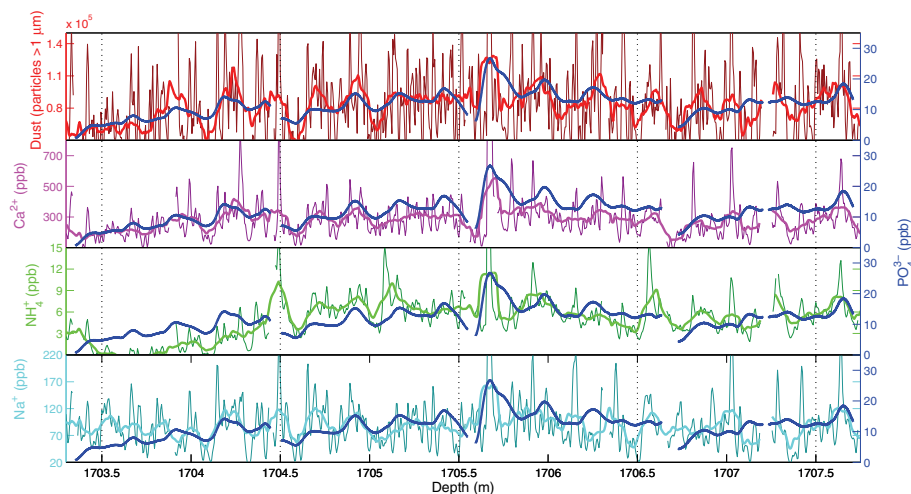


Fig. 6. High resolution CFA measurements from NEEM covering the transition to glacial interstadial 6, 1703.30 to 1707.75 m depth; PO_4^{3-} (blue), dust (red), Ca^{2+} (pink), NH_4^+ (green) and Na^+ (cyan). Thin and thick lines show the same data re-sampled at 0.5 cm and 5 cm depth resolution, respectively. The 0.5 cm resolution is provided, to compare timing of spikes, while 5 cm resolution shows the concentration level in a way that is more comparable to the level of PO_4^{3-} .

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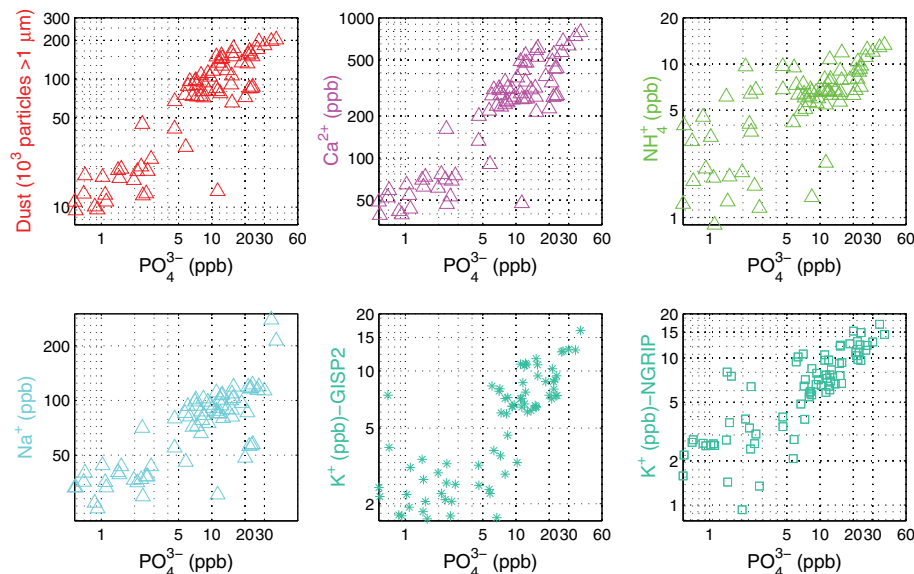


Fig. 7. Comparison of various CFA species determined in the NEEM ice core (triangles) and to K^+ determined with IC from the GISP2 ice core (stars) and NGRIP ice core (squares); 110 cm means are plotted against PO_4^{3-} 110 cm means. For K^+ -NGRIP (bottom, right) the 9 top excess spikes were removed from the K^+ before estimating means.

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